Docket No.:   240031US0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: GROUP: 1793
Mikio KONDOH, et al.

SERIAL NO: 10/615,939   EXAMINER: KESSLER

FILED: July 10, 2003

FOR: GREEN COMPACT AND PROCESS FOR COMPACTING THE SAME,
              METALLIC SINTERED BODY AND PROCESS FOR PRODUCING THE
              SAME, WORKED COMPONENT PART AND METHOD OF WORKING

DECLARATION UNDER 37 C.F.R. § 1.132

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

Sir:

Now comes _____ who deposes and states that:

1. I am a graduate of _____ and received my _____ degree in the year

_____.

2. I have been employed by Kabushiki Kaisha Toyota Chuo Kenkyusho for _____

years as a _____ in the field of _____.

3. The following experiments were carried out by me or under my direct supervision

and control. The Examples are the same as presented in the specification at pages 31-44,

including Table 1 and Figures 1-17 from the specification which are attached to this

Declaration and incorporated into the Declaration by reference.

(1) Examples

(Raw Material Powder)

Before mixing a raw material powder, five powders were first prepared as follows. A

pure titanium powder, a pure aluminum powder, an Al-6%Zn-2%Mg-1.5%Cu alloy powder, an

Al$_3$V powder and a TiB$_2$ powder were prepared. The pure titanium powder was produced by

WUYI Co., Ltd., and had an average particle diameter of 42 μm. The pure aluminum powder

was produced by FUKUDA KINZOKU HAKUHUN Co., Ltd., and had an average particle

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diameter of 30 μm. The alloy powder was produced by SUMITOMO KEIKINZOKU Co.,

Ltd., and had an average particle diameter of 35 μm. Note that the unit of the alloy

composition is expressed by % by mass (being the same hereinafter). The Al₃V powder was

produced by NIHON DENKO Co., Ltd., and had an average particle diameter of 20 μm. The

TiB2 powder was produced by NIHON SHINKINZOKU Co., Ltd., and had an average particle

diameter of 3.5 μm. Note that the TiB_2 powder corresponds to the hard-particle powder set

forth in the present specification.

Then, the powders were used independently, or were mixed appropriately, thereby

preparing active metallic powders having 5 compositions as set forth in Table 1.

(Preparation of Die Wall Lubricant)

As a surfactant, 6-grade polyoxyethylene nonyl phenyl ether (EO), 10-grade

polyoxyethylene nonyl phenyl ether (EO) and boric acid ester-based emulbon "T-80" (trade

name) were used. The three sufactants were mixed in a ratio of 1 : 1 : 1 by volume, and the

resulting mixture surfactant was contained in a proportion of 1.5% by volume in 100% by

volume water (i.e., a dispersion). Moreover, an antifoaming agent was added to the dispersion

in a proportion of 0.1% by volume. In addition, a lithium stearate (hereinafter abbreviated to

as "LiSt") powder was dispersed in an amount of 25 g with respect to the 100 cc water

including the mixture surfactant. The LiSt had a melting point of about 225 ℃, and had an

average particle diameter of 20 μm.

Then, the dispersion was subjected to a fine-pulverizing treatment with a ball-milling

pulverizing apparatus provided with polytetrafluorethylene-coated steel balls for 100 hours.

The resulting stock solution immediately after the fine-pulverizing treatment was diluted with

water and an ethyl alcohol-based solvent. In this instance, water was used in an amount of 14

parts by volume, and the ethyl alcohol-based solvent was used in an amount of 5 parts by

volume, respectively, with respect to 1 parts by volume of the stock solution. Hence, the ethyl

alcohol-based solvent was added in an amount of 25% by volume with respect to 100% by

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volume water. Thus, a die wall lubricant to be applied to the inner surface of a die was prepared.

(Die)

A die was prepared. The die was made of cemented carbide, and had a cylinder-shaped cavity whose size was φ 23.000 ± 0.005 mm × 50 mm. Moreover, an upper punch and a lower punch were prepared. The upper and lower punches were made of high-speed steel. The inner surface of the die was subjected to a TiN coating treatment in advance to exhibit a superficial roughness of 0.4Z. In addition, a band heater was wound around the die so that the die could be heated whenever appropriate.

(Compacting)

The die and the respective raw material powders were heated to 150 ℃. Note that the raw material powders were heated with an oven (i.e., an electric furnace) in air.

To the inner surface of the die which was heated to 150 ℃, the die wall lubricant was sprayed uniformly with a spraying gun at a rate of 1 cm³/sec. approximately. Thus, a lubricant film was formed on the inner surface of the die in a thickness of about 1.5μm (i.e., an applying step).

Into the die, the heated raw material powders were filled, respectively (i.e., a filling step). The raw materials were compacted by warm pressurizing while changing the compacting pressure in a range of from 392 to 1,568 MPa appropriately (i.e., a compacting step). Table 1 also summarizes the compacting pressures in the compacting step.

The upper and lower punches were actuated to eject the formed green compacts from the die, respectively (i.e., an ejecting step). The ejection forces in the ejecting step were also measured.

Moreover, the green compacts comprising the Ti-based powders were sintered in vacuum at 1,300 ℃ for 4 hours (i.e., a sintering step).

(2) Comparative Examples

As comparative examples, green compacts were produced with the pure titanium alloy and pure aluminum alloy and by compacting them at room temperature. In this instance, a commercially available dry fluorine lubricant "YUNON-S" (trade name) was used as a die wall lubricant, and was applied to the inner surface of the die by spraying in the same manner as the examples. The compacting pressure was controlled basically in such a range that the die was not damaged by galling and the like. Table 1 also summarizes the compacting pressures in the compacting operation.

(3) Measurements

The green compacts produced in the examples and comparative examples were examined for the green density and the ejection force, respectively. Table 1 also summarizes the results of the measurements. Moreover, Table 1 also summarizes the ratio (i.e., the relative density) of the green density with respect to the true density. Note that the true density was found by examining cast products, which had the same composition as those of the respective raw material powders, for the density. The green density was calculated from measured values which were obtained by measuring the weight and dimensions of the respective green compacts.

The ejection force was determined in the following manner. An ejecting load was measured with a load cell. The measured load was divided by the lateral area of the respective green compacts to determine the ejection force.

Moreover, regarding the metallic sintered bodies, the dimensional change occurred in the sintering step was determined by measuring the dimensions before and after the sintering step. The sintered-body density of the respective sintered bodies was measured by an Archimedes method.

(4) Assessment

(A) Examples Made of Titanium-based Raw Material Powder

(Examples Made of Pure Titanium Powder)

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The lines of Table 1 designated with Sample Nos. 1-1 through 1-6 and Sample Nos. C1-1 though C1-3 as well as Figs. 1 through 4 set forth the characteristics when the pure titanium powder was compacted by a variety of compacting pressures.

It is apparent from Table 1 and Figs. 1 through 4 that, in accordance with the present examples in which the pure titanium powder was warm compacted, high-pressure compaction was realized in which the pure titanium powder could be formed by a compacting pressure beyond 1,500 MPa. Thus, it was possible to provide a process for compacting an exceptionally high-density green compact.

Specifically, the green relative density was well over 85%, the conventional maximum level, and reached in a range of from 98 to 99%. Thus, green compacts were produced whose green density was virtually equal to the true density.

Note that the relative density is employed as an index of the green density in Table 1 as well as Fig. 1 and so on, because the true density depends on the composition. Thus, the relative density is employed in order to objectively assess the extent of high densification by the present compacting process. The discussion is similarly applicable to the sintered-body density.

When observing Fig. 2, it is apparent that, in the examples, the compacting pressure increased remarkably though the ejection force hardly varied. Moreover, when the compacting pressure was about to exceed 600 MPa, the ejection force decreased to such very low values as 5 MPa or less. In addition, when the compacting pressure exceeded 784 MPa, the ejection force was substantially constant at such an extremely low value as about 2.5 MPa.

On the other hand, in room-temperature compacted green-compacts of the comparative examples, galling occurred to the die when the compacting pressure was no more than 588 MPa. Moreover, the relative density of the produced green compacts did not reach even 85% at best. In addition, when the pure titanium powder was compacted at room temperature, the ejection force enlarged sharply in proportion to the increment of the compacting pressure substantially.

When observing Fig. 3, it is seen that the green density increased as the compacting pressure increased, and that the sintered-body density increased as the green density increased. In particular, in the present examples, when the green compacts which were compacted by the compacting pressure of 1,176 MPa or more were sintered, the density of the resulting sintered body increased virtually equal to the true density.

In addition, when observing Fig. 4, it is understood that the dimensional change before and after sintering was very small in the present examples so that it fell in a range of from about 1 to 3%. On the other hand, the comparative examples in which the pure titanium powder was compacted at room temperature, the original green compacts per se had a low density. Accordingly, the dimensional change before and after sintering was considerably large so that it fell in a range of from 4 to 10%.

(Examples Made of Titanium Alloy Powder)

The lines of Table 1 designated with Sample Nos. 2-1 through 2-3 and Sample Nos. 3-1 though 3-3 as well as Figs. 5 through 7 set forth the characteristics when the alloy mixture powder as well as the alloy mixture powder with the TiB_2 powder mixed were compacted by a variety of compacting pressures. Note that the alloy mixture powder was prepared by mixing the pure titanium powder with the Al_3V powder.

First, when the mixture powder whose alloy composition was Ti-6Al-4V was warm compacted, green compacts and metallic sintered bodies were produced whose green density and sintered body density were exceptionally high. In particular, the sintered body density stabilized at such a high value that the relative density was about 99.5% in all of Sample Nos. 2-1 through 2-3. Moreover, in Sample Nos. 2-1 through 2-3, the ejection force stabilized at such a low value that it was about 1 MPa or less.

Then, when the alloy mixture powder with the TiB_2 powder mixed was compacted by warm pressurizing, the resulting green compacts and metallic sintered bodies had a sufficiently large green density and sintered body density, and were ejected from the die by an adequately small ejection force. For example, when the compacting pressure was 1,176 MPa,

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the relative density of the green compact reached 94%, and the sintered-body density of the metallic sintered body arrived even at 99%. In this instance, the ejection force of the green compact was about 5 MPa or less in all of Sample Nos. 3-1 through 3-3.

Moreover, when the TiB_2 powder was mixed in an amount of 6% by mass, it is understood from Fig. 6 that an unusual phenomenon occurred that the ejection force decreased despite the enlarging compacting pressure.

However, when Sample Nos. 3-1 through 3-3, in which the TiB_2 powder was mixed, were compared with Sample Nos. 2-1 and 2-3 free from the TiB_2 powder, the densities were lower slightly and the ejection forces were somewhat higher for identical pressures. However, it seems that the density decrement and ejection force increment depend on the mixing amount of the TiB_2 powder. It is needless to say that all of the density and ejection-force values are remarkably good compared with the case where the alloy mixture powder with the TiB_2 powder mixed was compacted at room temperature.

Moreover, it is understood from Fig. 7 that all of Sample Nos. 2-1 through 2-3 and Sample Nos. 3-1 through 3-3 according to the present examples had a higher density than comparative samples did. Note that, in the comparative samples, the alloy mixture powder with the TiB_2 powder mixed was compacted by 392 MPa by means of CIP.

(B) Examples Made of Aluminum-based Raw Material Powder

(Examples Made of Pure Aluminum Powder)

The lines of Table 1 designated with Sample Nos. 4-1 through 4-7 and Sample Nos. C2-1 though C2-3 as well as Figs. 8 and 9 set forth the characteristics when the pure aluminum powder was compacted by a variety of compacting pressures.

The overall tendency of the characteristics was similar to Sample Nos. 1-1 through 1-6 in which the pure titanium powder was warm compacted. The green compacts according to the present examples had an extremely high density.

However, in Sample Nos. 4-1 through 4-7 according to the present examples, the ejection force was so low as about 1 MPa or less regardless of the compacting pressures.

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Namely, even when the compacting pressure was low, for example, when it was 392 MPa in Sample No. 4-1, the ejection force was low. When observing the column of Table 1, "Outside Dia. after Ejection," it is understood that the phenomenon seems to have resulted from the fact that the outside diameter of the ejected green compacts was as large as or slightly less than the inside diameter of the die. However, as can be seen from Table 1 and Fig. 9, no such tendency was not observed in Sample Nos. C2-1 through C2-3 in which the pure aluminum powder was compacted at room temperature.

(Examples Made of Aluminum Alloy Powder)

The lines of Table 1 designated with Sample Nos. 5-1 through 5-3 as well as Figs. 10 and 11 set forth the characteristics when the one and only aluminum alloy powder whose alloy composition was Al-6Zn-2Mg-1.5Cu was compacted by a variety of compacting pressures. The overall tendency of the characteristics was similar to Sample Nos. 4-1 through 4-7 in which the pure aluminum powder was warm compacted.

However, compared with Sample Nos. 4-1 through 4-7 in which the pure aluminum powder was warm compacted, the density of the resulting green compacts was lower slightly and the ejection forces were higher slightly for identical compacting pressures when the aluminum alloy powder was warm compacted. It seems that this phenomenon resulted from the fact that the aluminum alloy powder comprised particles which exhibited higher strength than the pure aluminum particles did so that the compressibility lowered. Regardless of the phenomenon, the relative density of the green compact reached 94% or more. Accordingly, it is understood that fully high-density green compacts could be produced. It is needless to say that all of the density and ejection-force values are remarkably good compared with the case where the aluminum alloy powder was compacted at room temperature.

(C) Metallic-Sintered Body

Made of Raw Material Powder with Increased Hard-Particle Content

The larger the TiB_2-powder content is, the resulting metallic sintered bodies can exhibit higher rigidity and strength. On the other hand, the larger the TiB_2-powder content is, the

more the formability and sinterability of green compacts lowers in general. Accordingly, in order to further assess the formability and sinterability according to the present compacting process and sintering process, a metallic sintered body was newly produced whose TiB_2-powder content was increased up to 12% by mass.

Except the TiB_2-powder content, a new sample, another example according to the present invention, was produced under the same conditions as those of Sample No. 3-3. Specifically, the titanium alloy mixture powder with the TiB_2 powder mixed was compacted with the die which was heated to 150 °C by a compacting pressure of 1,568 MPa, and thereafter the resulting green compact was sintered at 1,300 °C. Moreover, a comparative sample was produced in the following manner. A raw material powder having the same composition as that of the new sample was compacted by a compacting pressure of 588 MPa at room temperature in the above-described manner, and thereafter the resulting green compact was sintered at 1,300 °C.

Figs. 12 and 13 illustrate how the relative density and dimensional change of the present sample and comparative sample changed when the sintering time was varied, respectively. Note that the hard-particle content is expressed by 20% by volume TiB in the drawings, because the 12% by mass TiB_2 was turned into 20% by volume TiB by sintering.

First, as can be seen from Fig. 12, in the present sample, a sufficiently high-density green compacts were produced by sintering the raw material powder in an extremely short period of time, and the relative densities were close to 100%. On the other hand, in the comparative sample, it took a longer time to sinter the raw material powder in order to heighten the relative density of the resulting metallic sintered bodies. Note that, even when the raw material powder is pulverized to disperse a large amount of hard particles in the raw material powder, the conventional process like the comparative sample is considerably poor in terms of the powder formability and sinterability, and accordingly cannot produce metallic

sintered bodies whose density is as high as those of the metallic sintered bodies produced by the present sample.

Then, as can be understood from Fig. 13, in the present sample, the dimensional change was very small, i.e., 2% approximately, and stabilized thereat. On the other hand, in the comparative sample, the dimensional change decreased greatly as the sintering time prolonged, and did not stabilize at all.

Thus, in accordance with the present sample, it became evident that metallic sintered bodies can be produced which have a high density and are good in terms of the dimensional stability.

(D) Mechanical Characteristics of Metallic Sintered Body with Hard Particles Dispersed

A raw material powder including a TiB_2 powder was compacted by pressuring, and was further sintered to produce a metallic-sintered-body sample. The resulting sample was examined for the tensile strength and fatigue strength.

The composition of the used raw material powder was the same as that of Sample No. 3-3 recited in Table 1. The present sample was produced in the same manner as Sample No. 3-3. However, the present sample was formed as a shape of traverse test pieces whose size was 10 mm × 10 mm × 55 mm. A comparative sample was made by sintering a green compact, which was compacted as the identical shape by 392 MPa by means of CIP, at 1,300 °C. The comparative sample which was sintered for 4 hours was labeled as Comparative Example No. 1. The comparative sample which was sintered for 16 hours was labeled as Comparative Example No. 2. The resulting samples were processed into a tensile-test test piece and a rotating bending fatigue-test test piece. The respective test pieces were examined for the mechanical characteristics. Figs. 14 and 15 illustrate the result of the examinations. For reference, the hard-particle content is expressed by 10% by volume TiB in the drawings, because the 6% by mass TiB_2 was turned into 10% by volume TiB by sintering.

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The following are apparent from Figs. 14 and 15. The metallic sintered bodies of the present sample had an exceptionally higher sintered-body relative density than those of Comparative Example Nos. 1 and 2. Moreover, it was verified that the metallic sintered bodies of the present sample were remarkably better than those of Comparative Example Nos. 1 and 2 in terms of all of the tensile strength, elongation and fatigue strength

(E) Results of Superficial Analysis on Green Compacts according to the Present Invention

The surface of the green compacts of Sample Nos. 1-4 and 4-5 recited in Table 1 was analyzed by TOF-SIMS, respectively. Note that the green compact of Sample No. 1-4 was made of the pure titanium powder, and the green compact of Sample No. 4-5 was made of the pure aluminum powder. Figs. 16 and 17 illustrates secondary ion images produced as a result of the analysis.

From the drawings, it was confirmed that, for both of Sample Nos. 1-4 and 4-5, the distribution of stearic acid resembled the distribution of Ti or Al rather than the distribution of Li. It seems that the result suggests that a mechanochemical reaction occurred to form a new metallic soap film, which are believed to be titanium stearate or aluminum stearate, on the surface of the green compacts in the compacting step according to the present examples.

Please see the attached Figure 1 and Figures 1-17.

4. The undersigned petitioner declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

5. Further deponent saith not.

Mikio Kondoh

Signature

13. March 2008

Date

TABLE 1

Sample No.		Composition (% by mass)	Compaction Pressure (MPa)	Ejection Force (MPa)	Green Compact		Outside Dia. after Ejection (mm)	Metallic Sintered Body			Note
					Green-compact Density (g/cm³)	Relative Density (%)		Sintered-body Density (g/cm³)	Relative Density (%)	Dimension Change before and after sintering (%)	
Ex.	1-1	Pure Ti	588	3.5	4.025	89.2	23.059	4.325	95.9	-2.60	
	1-2		784	1.9	4.193	93.0	23.061	4.384	97.2	-1.59	
	1-3		980	2.4	4.292	95.2	23.065	4.451	98.7	1.37	Mixture Powder of Pure Ti Powder and Alloy Powder
	1-4		1176	2.5	4.364	96.8	23.070	4.496	99.7	-1.11	
	1-5		1372	2.6	4.391	97.4	23.075	4.501	99.8	-0.87	
	1-6		1568	2.2	4.422	98.0	23.079	4.505	99.9	-0.60	
	2-1	Ti-6Al-4V	784	0.9	3.991	91.1	23.065	4.403	99.3	-3.26	
	2-2		1176	0.5	4.201	95.9	23.071	4.407	99.4	-1.61	
	2-3		1568	0.5	4.285	97.8	23.081	4.412	99.5	-0.96	
	3-1	Ti-6Al-4V+6TiB₂	784	5.1	3.956	90.2	23.072	4.332	97.4	-3.04	Mixture Powder of said Mixture Powder and Hard-particle Powder TiB₂: 6t by mass
	3-2		1176	3.6	4.143	94.3	23.078	4.395	98.8	-2.06	
	3-3		1568	2.7	4.234	96.5	23.083	4.412	99.2	-1.46	
	4-1	Pure Al	392	0.3	2.611	96.8	22.997	-	-	-	
	4-2		588	0.7	2.656	98.4	22.992	-	-	-	
	4-3		784	0.7	2.672	99.0	22.994	-	-	-	
	4-4		980	0.7	2.686	99.4	22.994	-	-	-	
	4-5		1176	0.8	2.686	99.5	22.993	-	-	-	
	4-6		1372	0.8	2.667	99.8	22.994	-	-	-	
	4-7		1568	0.5	2.667	99.8	22.995	-	-	-	
	5-1	Al-6Sn-2Mg-1.5Ca	588	1.3	2.616	93.4	23.014	-	-	-	Equivalent to JIS A7475
	5-2		980	1.3	2.741	97.9	23.029	-	-	-	
	5-3		1568	1.4	2.794	99.8	23.038	-	-	-	
Comp. Ex.	C1-1	Pure Ti	294	8.0	3.209	71.2	23.068	4.235	93.9	-9.58	Room-temp. Compaction
	C1-2		441	16.3	3.521	78.1	23.075	4.290	95.1	-6.94	
	C1-3		588	24.1	3.728	82.9	23.082	4.300	95.3	-4.95	
	C2-1	Pure Al	392	4.1	2.583	95.7	23.056	-	-	-	Room-temp Compaction
	C2-2		588	5.7	2.615	96.9	23.057	-	-	-	
	C2-3		784	6.5	2.640	97.8	23.059	-	-	-	

Fig.1

Fig.2
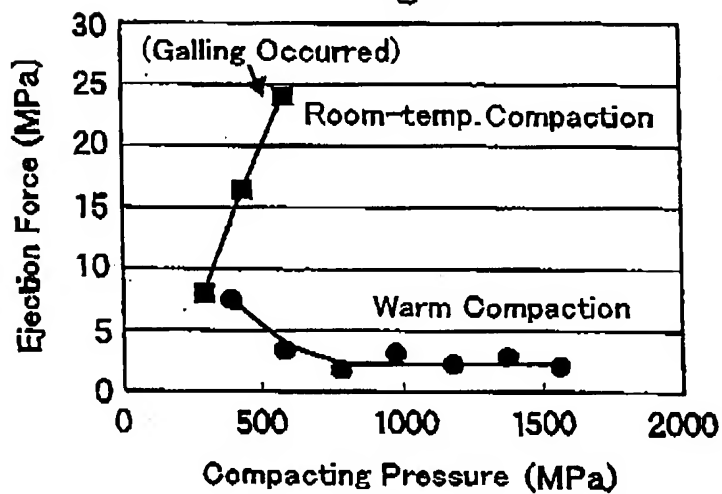
Fig.3
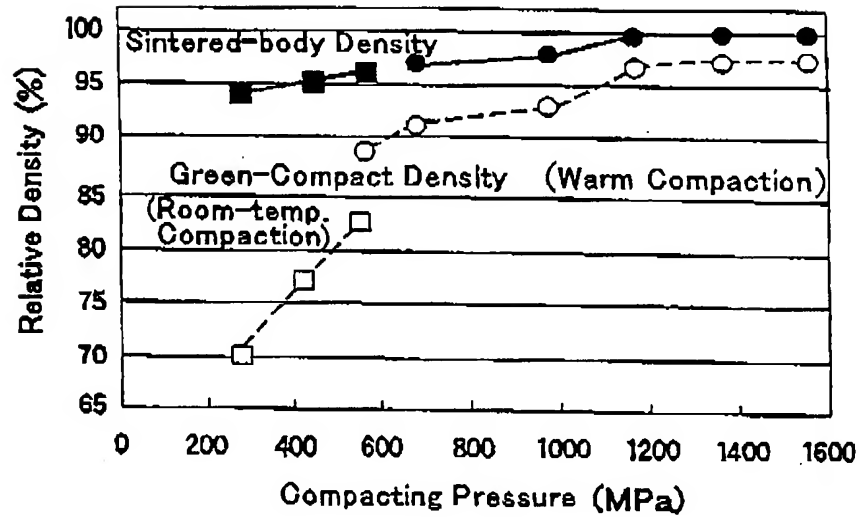
Fig.4
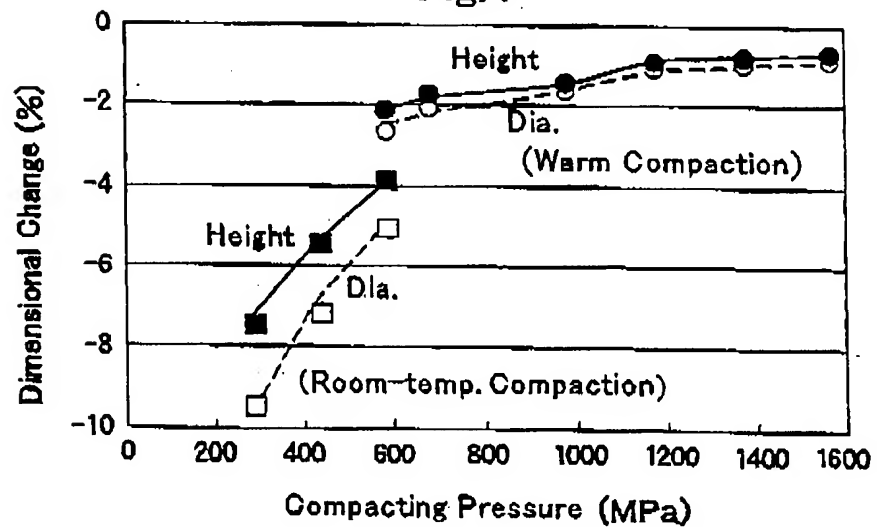
Fig.5
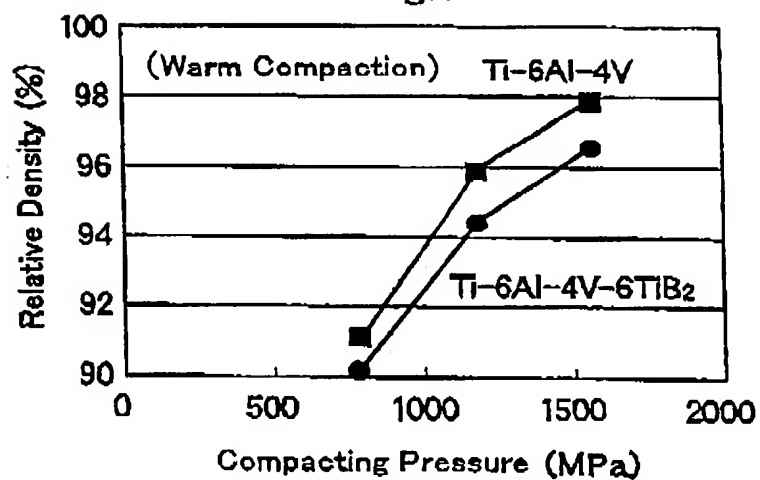
Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

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Fig.11

Fig.12

20vol%TiB/Ti-6Al-4V

Fig.13

20vol%TiB/Ti-6Al-4V

Fig.14

(10vol.%TiB/Ti-6Al-4V)

	Comp.Ex.No.1	Comp.Ex.No.2	Ex.
	CIP Forming 392MPa at Room Temp. Sintering Condition: 1300°C for 4hr.	CIP Forming 392MPa at Room Temp. Sintering Condition: 1300°C for 16hr.	Forming with Lubricated Mold 1,568MPa at 150°C Sintering Condition: 1300°C for 4hr.

Fig.15

(10vol.%TiB/Ti-6Al-4V)

Ex.1
Relative Density:99%
Fatigue Strength:375MPa

Comp.Ex.1 Relative Density Ratio:94%
Fatigue Strength:275MPa

Number of Cycles (times)

FIG.16

Ti   Li   Stearate

After Ultrasonic Washing, Size: 200 μ m × 200 μ m

FIG.17

Al   Li   Stearate

As Formed, Size: 200 μm × 200 μm